

PATENT SPECIFICATION

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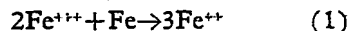
(54) ELECTROCHEMICAL CELL FOR QUANTITATIVE ANALYSIS

(71) We, SOCIÉTÉ CENTRALEC, a French Body Corporate, of Chemin de Marcy, 58 800 Corbigny, France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a cell for electrochemically checking and measuring the ion concentration of a solution, independently of the nature of the solvent, and is of use more particularly for checking the concentration of pickling or scouring or electrodeposition baths. The invention is also of use in all cases where the changes in a given solution have to be measured continuously or intermittently or where the uniformity of its concentration has to be checked without manipulating the solution itself, more particularly without taking and destroying samples.

It is known, for example, that the high concentration of pickling or electrodeposition baths and the temperature at which they are used, makes it extremely difficult to operate them with sufficient accuracy on an industrial scale, since conventional methods of checking are usually based on measurements of pH or electric conductivity.

The object of the invention is to obviate the disadvantages of the conventional methods. A non-limitative embodiment will be described in detail hereinafter, with reference to its application to checking and measuring iron ions in a FeCl₃-based aqueous solution for chemical machining. It is known that, in the case of iron, the chemical machining of components, i.e. the removal of metal, theoretically corresponds to the following redox reaction:



If the machining solution or bath comprises a solution of ferric chloride (FeCl₃), the complete reaction is as follows:



During machining, therefore, the bath becomes enriched in ferrous chloride, accompanied by a reduction in its oxidizing power. Curves I and II, which are illustrated in the accompanying Figure 1 and wherein the abscissae show the inter-electrode potential of a pair of electrodes in the bath and the ordinates show the current flowing between the electrodes, are characteristic of the redox reactions of the Fe⁺⁺/Fe⁺⁺⁺ systems in the presence of chloride, or, more precisely, the kinetics of these reactions, since the current is proportional to the exchange rate of the electrons at the electrode-solution interfaces. If certain precautions are taken, curves (I) and (II) show plateaux where the current is proportional to the ion concentration, the mass transfer occurring by a diffusion process.

In Figure 1, therefore, curve (I) corresponds to the reduction of Fe⁺⁺⁺ ions and curve (II) corresponds to the oxidation of Fe⁺⁺ ions. Curve (III), which shows the sum of curves (I) and (II), has been drawn for a mixture of equal volumes of the two species of ions. The range of potential which may be used is limited at about -1.5V by the reduction of the protons of the solution and towards +1.4V by the oxidation of the chloride. As the drawing shows, the current is substantially proportional to the concentration of Fe⁺⁺ for a potential difference of about 0.8V between the electrodes.

Accordingly, the invention relates to a cell for checking ionic solutions in order continuously to measure the kinetics of the redox reaction occurring at the surface of two indicating electrodes operating at a constant voltage, the value of which depends on the nature of the ions to be checked.

To this end, the cell is characterised in that it comprises two identical electrodes immersed in the solution, means for maintaining a constant voltage between the electrodes within a range where the current estab-

lished between the electrodes is substantially constant at constant concentration of an ion species in the solution, means for agitating the solution to provide a constant flow rate between the electrodes and means for measuring the current established between the electrodes.

Other features and advantages of the measuring cell according to the invention will be clear from the following description, which refers to the accompanying drawings of a number of exemplary non-limitative embodiments of the cell. In the drawings:

Figure 2 shows an analytical cell according to the invention, in axial longitudinal section;

Figure 3 shows an alternative embodiment of one of the cell electrodes;

Figures 4a, 4b and 4c show families of curves which can be read off to show the concentration of the solution based on the values of the currents supplied by the cell; and

Figure 5 shows another alternative embodiment of the cell of the invention.

The cell, as diagrammatically shown in Figure 2, essentially comprises a sealing-tight chamber 1 surrounding an asynchronous electric motor 2, a measuring compartment 3 adapted to be immersed in the ionic solution in question and containing a turbine wheel 4 at its bottom, two identical indicating electrodes 5 and 6, and an intermediate part 7 through which a titanium shaft 8 extends and is guided in rotation by polytetrafluoroethylene bearings 9 and 10, the shaft 8 enabling the turbine wheel 4 to be driven by motor 2 and being connected thereto by a flexible coupling 11. The turbine wheel 4 is made of a plastics material, for example perchlorinated polyvinylchloride.

In a simplified embodiment, electrodes 5 and 6, the bottom ends of which are situated in the same plane, are formed by inserting a vitreous carbon cylindrical rod 12 into an insulating tubular holder 12a. The electrodes are subjected to a constant voltage, e.g. of about 0.8V. In each electrode, rod 12 is connected to an electric wire 13 by a drop of mercury 14, the assembly being sealed. Advantageously electric wire 13 is made of molybdenum, which does not form an amalgam with mercury. The two electrodes are disposed at equal distances from the longitudinal axis of the apparatus. The fact that the cylindrical rod 12 is made of vitreous carbon ensures that the electrochemical reactions are stable, so that the results are reproducible. Alternatively, as shown on a larger scale in Figure 3, the vitreous carbon rod 12 of the electrode shown is an electrical contact via a mercury drop with a metal intermediate rod 13a made of tungsten and which is connected to the end of rod 13 by a weld 13b, for example a silver weld. The rods 13 and 13a are held along the axis of holder 12a and

the device is sealed from the exterior by two seals 21 and 22, seal 21 being a short distance above the mercury drop 14 and seal 22 being at that end of the holder remote from rod 12, the seals being made of suitable synthetic resins.

Two coaxial tubes 15, 16 secured to a base 18 together bound an annular duct 17 communicating with the outside of the measuring compartment 3 via an orifice 19, whereas a duct 20 connects the interior of tube 15 to outside compartment 3. The materials used for the various components of the cell preferably include titanium, polytetrafluoroethylene, or polyvinyl chloride where suitable, since these materials are inert to most chemical substances and the maximum operating temperature of the cell can be relatively high, at least about 105°C.

Accordingly, the cell according to the invention operates as follows. The measuring compartment 3 is immersed in the bath or solution to be studied, after which electric motor 2 is started to drive turbine wheel 4 via shaft 8. The wheel drives a turbulent flow of solution, so that the bath to be analyzed flows through orifice 19 into annular duct 17 (arrow F1), then through a duct 21 supplying the turbine wheel 4 and into that wheel (arrow F2), then from wheel 4 into compartment 3 (arrow F3) and finally out of compartment 3 via duct 20 (arrow F4).

The inlet orifice 19 and the discharge duct 20 are in a single plane perpendicular to the longitudinal axis of the apparatus and turbine wheel 4 ensures a forced, regular flow of the bath so that said flow is irrespective of the level at which the cell is immersed in the bath.

In order, therefore, to know the concentration of the baths in which the measuring compartment 3 is immersed, it is merely necessary, according to the features explained hereinbefore, to read off the current flowing between electrodes 5 and 6, and knowing the temperature of the bath under study, to read the concentration corresponding to the read-off current on the curve in Figure 4c corresponding to the bath temperature.

Figures 4a and 4b show a family of curves, for each species of ion in solution and for a given bath temperature, each curve corresponding to a known given concentration, the curves indicating the variations in the current measured between the electrodes in dependence on the voltage between the electrodes. As can be seen, each of the aforementioned curves has a relatively long plateau. In Figure 4a, the example, curves I, II, III and IV correspond to current values read off in dependence on the voltage for Fe ions at concentrations of 0 g/l, 1 g/l, 2 g/l and 4 g/l respectively, the bath temperature being 20°C.

Similarly, in Figure 4b, curves I', II', III', 130

IV' give the value of the current in dependence on the voltage for Fe ions at concentrations respectively of 0 g/l, 1 g/l, 2 g/l and 3 g/l, the bath temperature being 60°C. In practice, the number of curves drawn may be much greater than four.

If, under the aforementioned conditions, a line is drawn in Figure 4a parallel to the ordinate axis and intersecting the plateaux of the different curves and the ordinates of the points of intersection read off, the values read off can be used to draw curve A on Figure 4c, representing variations in current in dependence on the concentration for a given voltage. It is found by experience that curve A is substantially a straight line, except near the origin. The curve corresponds to a bath at a temperature of 20°C.

Using Figure 4b, the same method yields a curve B on Figure 4c corresponding to a bath at a temperature of 60°C.

The cell according to the invention is used as follows, in accordance with the family of curves drawn in Figure 4c. The solution is immersed in a FeCl_3 -based chemical machining bath at a temperature of e.g. 20°C, and a current of N milliamps is read off. It is then merely necessary to draw a line on Figure 4c parallel to the abscissa axis through ordinate N, the parallel line intersecting curve A, corresponding to a temperature of 20°C, at a point Q whose abscissa OP measures the desired concentration of Fe^{++} ions in the machining bath.

The cell according to the invention can be used for electrochemical testing free from the difficulties occurring in the prior art, more particularly by avoiding any taking or destruction of samples. Owing to its construction and its small volume, the cell can be used under a variety of conditions. More particularly, it is found that it supplies the same readings in a 500 cm³ beaker as in a 300-litre bath, independently of the degree of immersion and with short response times, and the results being independent of the hydrodynamic conditions outside the cell. Furthermore, owing to the regularly-maintained motion of the liquid between the electrodes, the measurements are stable and essentially reproducible.

Finally, if a number of cells according to the invention are used, the cells provide signals differing only by a proportionality factor K. They can then be calibrated, in a standard solution, using a simple potentiometer, and the constant K can be defined. By means of a voltage switching device, e.g. a rotary manual switch, the same cell can be used to check different species of ions in a single bath, provided an inter-electrode voltage for each species is applied, corresponding to the redox reaction of the species in question. In all cases, of course, the voltage should be compatible with the stability of the solvent.

Of course, the invention is in no way limited to the embodiment described in detail and shown hereinbefore, but includes all variants within the scope of the Claims. More particularly, the flow of the bath into the measuring compartment of the cell can be ensured by any suitable means equivalent to the aforementioned centrifugal turbine.

For example, in the case where measurements are to be made, not by immersing the cell in a bath, but by immersing it in a flow of the solution under test, the cell may be mounted as shown by the view in section in Figure 5, on a duct element 30 provided with two end flanges 31, 32 for securing it to piping containing the flow. The cell chamber 33 extends through duct 30 so that electrodes 5, 6 are disposed substantially at the centre of the flow of solution travelling through the duct in the direction shown by the arrows, the electrodes being connected by connecting wires 5a, 6a to an external measuring device (not shown). In the last-mentioned embodiment, the solution is agitated in the neighbourhood of the electrodes not by a turbine wheel but by a static device such as a convergent-divergent venturi tube, which can speed up the flow and ensure a constant flow rate at the neck 35 of the pipe where the electrodes are situated, thus providing the necessary conditions of stability and reproducibility of measurements. The device can be supplemented, if required, by an inspection stopper 36 and a thermometer 37 for measuring the temperature of the solution.

WHAT WE CLAIM IS:—

1. A cell for electrochemically checking or measuring the concentration in ions of a solution, characterised in that it comprises two identical electrodes immersed in the solution, means for maintaining a constant voltage between the electrodes within a range where the current established between the electrodes is substantially constant at constant concentration of an ion species in the solution, means for agitating the solution to provide a constant flow rate between the electrodes and means for measuring the current established between the electrodes.

2. A cell according to Claim 1, characterised in that it comprises a voltage switching device to change the voltage maintained between the electrodes for checking or measuring the concentration of two or more ion species in a single bath.

3. A cell according to Claim 1, wherein the solution is a FeCl_3 -based aqueous solution for electrochemical machining and characterised in that the active part of the electrode is made of vitreous carbon, the voltage applied between the electrodes being of about 0.8V.

4. A cell according to Claim 1, charac-

- terised in that the means for agitating the solution comprise a centrifugal turbine.
5. A cell according to Claim 1, characterised in that it is made of chemically inert substances adapted to withstand a temperature of about 105°C at least.
6. A cell according to Claim 1, characterised in that each electrode comprises a vitreous carbon rod mounted in a tubular holder and connected by a drop of mercury to a molybdenum wire providing an electric connection.
7. A cell according to Claim 6, characterised in that the connection between the connecting wire and the mercury drop is provided by a tungsten rod which is immersed in the drop and which is connected to the wire by a silver weld.
8. A cell according to Claim 1 characterised in that the means for agitating the solution comprise a convergent-divergent tube, the measuring electrodes being disposed in the neighbourhood of the neck of the tube.
9. A cell for electrochemically checking and measuring the concentration in ions of a solution substantially as hereinbefore described and as shown in the accompanying drawings.
10. A method of electrochemically checking or measuring the concentration in ions of a solution which method comprises immersing two identical electrodes in the solution, maintaining a constant voltage between the electrodes within a range where the current established between the electrodes is substantially constant at constant concentration of an ion species in solution, agitating the solution so that at least a portion thereof passes between the electrodes at a constant flow rate and measuring the current established between the electrodes.
11. A method as claimed in Claim 10 wherein the progress of a redox reaction is checked.
12. A method as claimed in Claim 11 wherein the redox reaction is electrochemical machining using a FeCl_3 -based aqueous solution and the voltage applied between the electrodes is about 0.8V.
13. A method as claimed in Claim 10 substantially as hereinbefore described.
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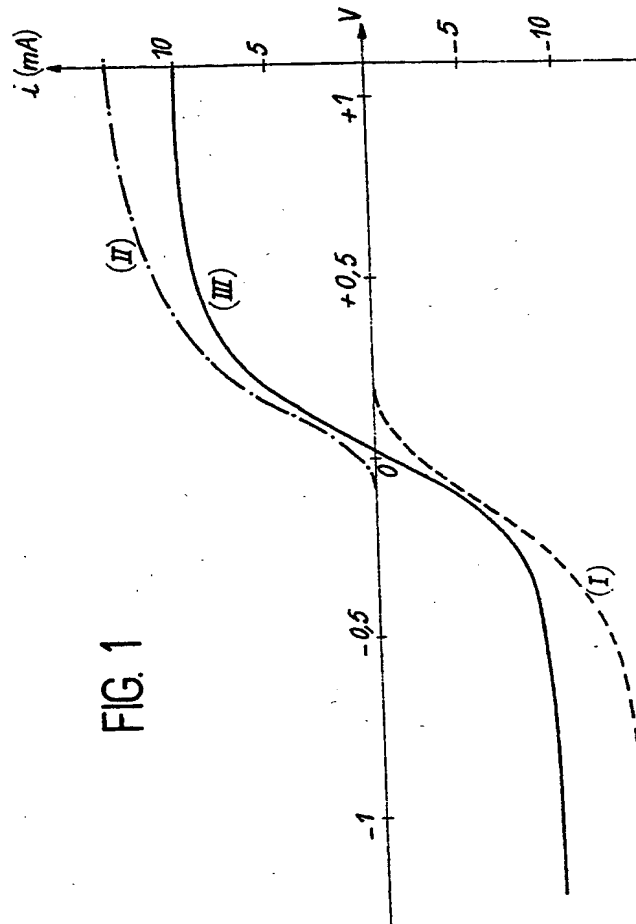


FIG. 1

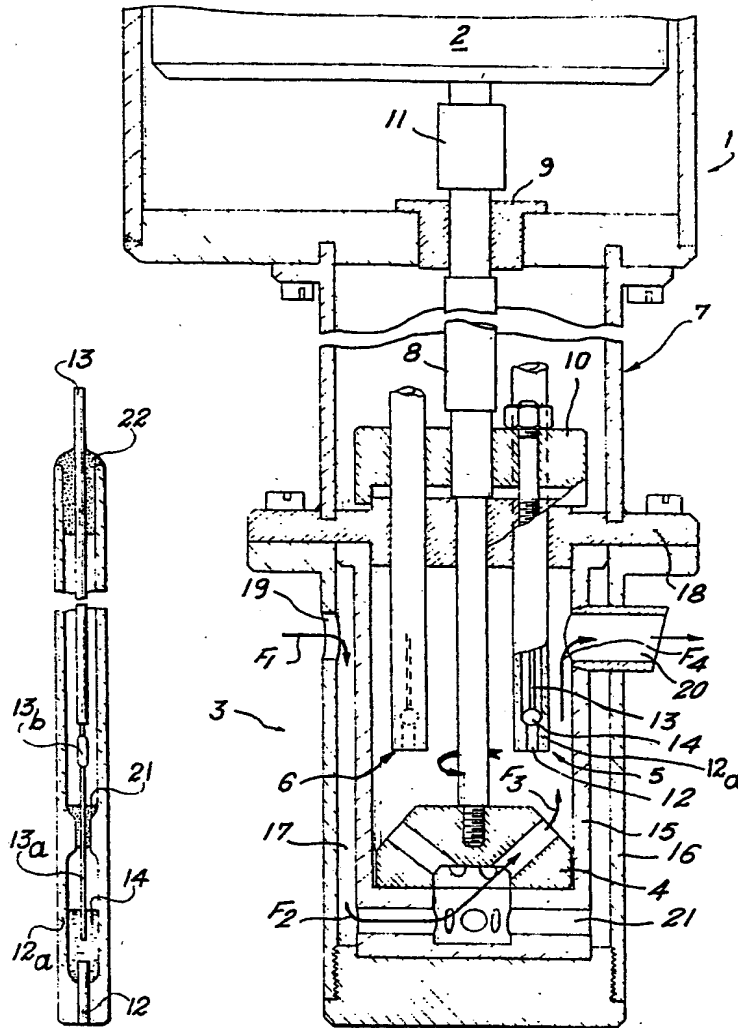


FIG. 3

FIG. 2

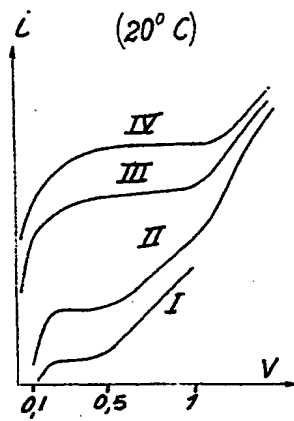


FIG. 4a

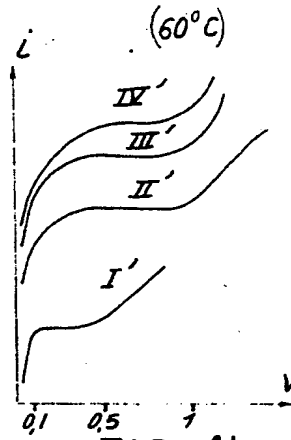


FIG. 4b

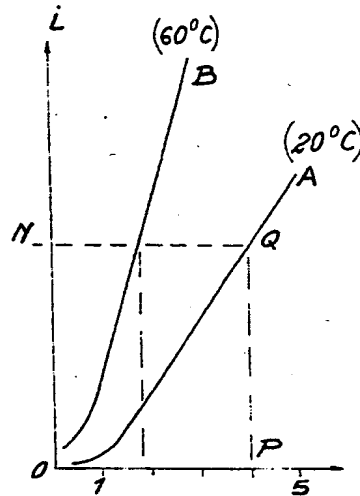


FIG. 4c

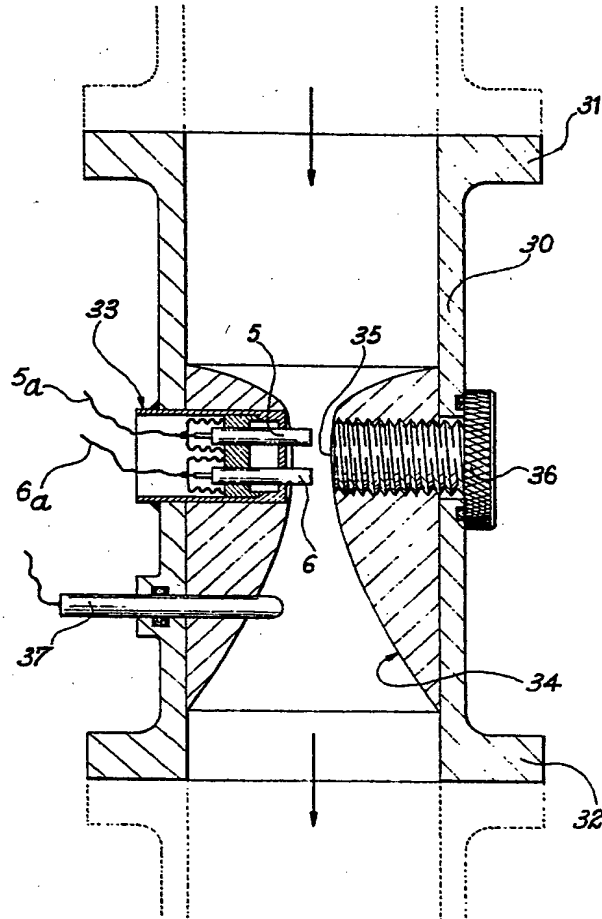


FIG. 5